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(54) **Surgical adhesive sheet**
Chirurgische Heftfolie
Feuille adhésive chirurgicale

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Description

BACKGROUND OF THE INVENTION

1. Field of the Invention:

This invention relates to application of surgical adhesive. More particularly, it relates to application means, instruments and methods, for surgical adhesive comprising an NCO-terminated prepolymer

2. Description of the Prior Art:

As surgical adhesives, there have been known heretofore those comprising a hydrophilic urethane prepolymer prepared by reaction of organic polyisocyanate with polyether polyol (for example, JPN Patent Lay-open No. 148666/1987 = US Patents 4,740,534 and 4,806,614).

Such adhesives comprising prepolymer, however, have drawbacks that, due to their high viscosity and high adhesive power, they are of poor handleability, that it is difficult to apply only a necessary amount to a fixed place to be bound, and use of adhesives in an amount more than needed causes adhesion with other part of living tissue and gets into trouble other than treatment purpose, and that they must be used quickly because such prepolymer is rapidly cured by reaction with water or body fluid on tissue surface .

In bonding of arterioles with surgical adhesives, vessel is bonded in collapsed state to result in obliteration of vessel.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide application means of surgical adhesive comprising NCO-terminated urethane prepolymer, with improved handle-ability.

It is another object of this invention to provide a surgical adhesive manufactured in the form easily handled for bonding tissue.

According to the invention there is provided a surgical adhesive sheet comprising an anhydrous sheet material coated with a surgical adhesive comprising an NCO- terminated urethane prepolymer.

Preferred surgical sheets according to the invention comprise a non-absorbing sheet material comprising at least one polymer being at least one of olefinic polymers, acrylic and methacrylic resins, hydroxyl-containing polymers, halogen-containing resins, diene polymers, polyesters, polycarbonates, polyamides, polyimides, polyurethane resins and silicone resins.

Surgical sheets according to the invention may be in the form of a film, plate or balloon.

The invention will be further described, by way of example with reference to the drawings in which:

Figure 2 is a schematic representation of a process of haemostasis using a surgical sheet according to the invention;

Figure 3 is a schematic representation of a process of haemostasis using a surgical sheet according to the invention in the form of a balloon;

Figure 6 is a schematic representation of a process of anastomosis of a vessel.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Suitable sheet materials, for use in producing said surgical adhesive sheet of the present invention, include non-biodegradable ones and biodegradable ones.

Illustrative examples of non-biodegradable sheet materials are those of polymers, including those obtainable by addition polymerization, for instance, olefinic polymers (such as polyethylenes, ethylene copolymers, polypropylenes, polybutenes and the like), acrylic and methacrylic resins (such as polymers and copolymers of acrylate, methacrylate or/and acrylonitrile), hydroxyl-containing polymers (such as polyvinyl alcohols), halogen-containing polymers (such as vinyl chloride resins, polyvinylidene chlorides, fluorine-containing resins, rubber hydrochlorides and chloroprene polymers), diene polymers (such as butadiene polymers and isoprene polymers), and the like; and polycondensation polymers, for example, polyesters, polycarbonates, polyamides, polyimides, polyurethane resins, silicone resins, and the like. Among these, preferred are polyurethane resins, silicone resins and fluorine-containing resins.

Biodegradable sheet materials include, for example, those of natural and synthetic polymers written in WO 84/03035 (JPN Tokuhyo Sho60-500485). Exemplary of biodegradable natural polymers are partially oxidized celluloses, chitin and derivatives thereof, collagen and derivatives thereof, and the like. Suitable biodegradable synthetic polymers are inclusive of polyamino acids, polyamino acid copolymers and delivatives thereof, polylactic acids, polyglycolic acids, copolymers of lactic acid and glycolic acid, polymers of hydroxybutyric acid, and so on. Among these, preferred are polyamino acids, polyamino acid copolymers and delivatives thereof, polyglycolic acids, copolymers of lactic acid and glycolic acid.

Two or more of these polymers may also be used.

Sheet materials in this invention can be in various forms, for instance, continuous films; films having a plurality of openings therein; and porous sheets, such as non-woven and woven fabrics, and the like.

Sheet materials may be usually 5 µm - 10 mm thick, closely depending upon the form. According to the part to be applied, application method and object, there can be taken various combinations of forms and thickness of sheet materials.

In case of films having openings or porous sheets, the surface may be laminated with water vapor-permeable and air-permeable films (such as silicone resin film,

polyurethane resin film and the like), having no permeability to micro-organisms (such as bacteria), to prevent infection.

Suitable surgical adhesives usable in the invention include ones comprising NCO-terminated urethane prepolymer.

As such prepolymer for adhesive used in this invention, preferred are NCO-terminated hydrophylic urethane prepolymers, derived from at least one organic polyisocyanate (a) and at least one hydrophilic polyether polyol (b) with or without one or more other polyols (c). Suitable examples of these prepolymers and the raw materials (a), (b) and (c) are those written in US Patent 4,806,614 and EP Patent 332,405.

Suitable polyisocyanates (a) include aromatic polyisocyanates containing 6 - 20 carbon atoms [such as tolylene diisocyanate (TDI), diphenylmethane diisocyanate (MDI), p-phenylene diisocyanate (PPDI) and the like], aliphatic polyisocyanates containing 2 - 18 carbon atoms, alicyclic polyisocyanates containing 4 - 15 carbon atoms, araliphatic polyisocyanates containing 8 -15 carbon atoms, except carbon atoms in NCO groups, and modified polyisocyanates of these polyisocyanates containing one or more of urethane, carbodiimide, allophanate, urea, biuret, urethdione, urethimine, isocyanurate and oxazolidone groups, as described in US Patent 4,806,614; and fluorine-containing polyisocyanates, as written in EP Patent 332,405, such as those represented by the general formula: OCN-Rf-NCO or OCN-CH_2-Rf-CH_2-NCO (wherein Rf represents perfluoroalkylene group containing 1 - 20 carbon atoms, which may contain one or more ether linkages). Among these polyisocyanates, preferred are fluorine-containing ones.

Suitable hydrophilic polyether polyols (b) include adducts of ethylene oxide [hereinafter referred to as EO] or combinations thereof with one or more other alkylene oxides [hereinafter refferred to as AO] to one or more compounds containing at least two active hydrogen atoms, for example, polyhydric alcohols (such as ethylene glycol, propylene glycol, and the like), polyhydric phenols, polyester polyols, amines, polycarboxylic acids, phosphorous acids and the like. Addition of EO or combination of EO with AO [random-addition, block-addition or combination of them (such as random-addition followed by block-addition)] to active hydrogen atom-containing compounds can be carried out in the usual way, with or without catalysts [such as alkaline catalysts, amine catalysts and acidic catalysts], under normal or an elevated pressure, in a single step or multi-stages. Hydrophilic polyether polyols have equivalent weight (molecular weight per hydroxyl group) of usually 100 - 5,000, preferably 200 - 3,000, and oxyethylene content of usually at least 30 %, preferably 50 - 90 % by weight. Content of the primary hydroxyl groups of polyether polyols is preferably at least 30 %, more preferably at least 50 %, most preferably at least 70 %.

Other polyols (c) include low molecular weight polyols and/or hydrophobic polyols. Examples of such polyols are polyhydric alcohols mentioned above [as raw materials for (b)]; AO adducts (such as propylene oxide adducts) of active hydrogen atom-containing compounds as mentioned above (polyhydric alcohols and others); and polyester polyols [for example, condensation products of dihydric and/or trihydric alcohols (such as ethylene glycol, propylene glycol, 1,3- and 1,4-butane diols, 1,6-hexane diol, neopentyl glycol, diethylene glycol, glycerol, trimethylolpropane and the like) and/or polyether polyols (such as those described above) with dicarboxylic acids (aliphatic or aromatic dicarboxylic acids, such as glutaric, adipic, sebacic, fumaric, maleic, phthalic and terephthalic acids) or ester-forming derivatives thereof (anhydrides and lower alkyl esters, such as maleic and phthalic anhydrides, dimethyl terephtharate, and the like); ring-opening polymerization products of lactones [such as epsilon-caprolactone]. Among these polyols, polyether polyols are preferred.

These polyols [(b) and optionally (c)], used for producing NCO-terminated urethane prepolymer, have equivalent weight(average) of usually 100 - 5,000, preferably 200 - 3,000 and usually 2 - 8 hydroxyl groups, preferably 2 - 4 hydroxyl groups.

In reacting at least one polyisocyanate (a) with at least one hydrophilic polyether polyol (b) and optionally one or more other polyols (c) to form NCO-terminated hydrophlic urethane prepolymers, ratio of NCO/OH is usually 1.5 - 5.0, preferably 1.7 - 3.0. The reaction of (a) with (b) and optionally (c) forming prepolymers can be performed in the usual manner. The reaction may be carried out in the presence of a catalyst. Prepolymers may be prepared by reacting (a) with a mixture of (b) and (c), or reacting successively in any order with (b) and (c). Prepolymers may be prepared by blending a prepolymer from (b) with a prepolymer from (c) [for instance, blending with a prepolymer from a low molecular weight polyol (equivalent weight 50 - 500) to reduce viscosity].

Preferable prepolymers are NCO-terminated hydrophylic urethane prepolymers, as described above; but, in stead of or in conjunction with such hydrophilic prepolymer, there may also be used other NCO-terminated urethane prepolymers, such as those derived from at least one organic polyisocyanate (a) with one or more other polyols (c), polyamines and the like. Examples of these the raw materials (a), (c), polyamines and the like include those written in "Handbook of Polyurethane Resins" (published 1987 by Nikkan Kogyo Shinbunsha) and also in US Patent 4,806,614 and EP Patent 332,405. These prepolymers can be produced in the same manner as hydrophilic prepolymers mentioned above, except that (b) is not used.

NCO-contents of NCO-terminated hydrophilic prepolymers are usually 1 - 10%, preferably 2 - 8 % by weight.

In surgical adhesives used in this invention, urethane prepolymers can be used in combination with other adhesive components, for example, unsaturated cyano compound containing cyano group attached to a carbon atom constituting the polymerizable double bond,

such as cyano(meth)acrylic acids and esters thereof, as described in US Patent 4,740,534.

Surgical adhesives used in this invention may contain, if necessary, one or more other components, for example, physiologically active mateials or medicinal drugs [such as agents affecting central nervous system, antiallergic agents, cardiovascular agents, agents affecting respiratory organs, agents affecting digestive organs, hormone preparations, agents affecting metabolism, antitumor agents, antibiotic preparations, chemotherapeutics, antimicrobias, local anesthetics, antihistaminics, antiphlogistics, astringents, vitamins, antifungal agents, peripheral nervous anesthetics, vasodilators, crude drug essences, tinctures, crude drug powders, hypotensive agents, and the like], fillers [for example, carbon black, metal oxides, such as red iron oxide and titanium dioxide, silicates, such as calcium silicates and sodium silicates, acrylic resin powders, various ceramic powders, and the like]; softening agents [such as DBP (dibutylphosphate), DOP (dioctylphosphate), TCP (tricresyl-phosphate), tributoxyethylphosphates, and other esters of various types]; stabilizers, such as trimethyldihydroquinone, phenyl-beta-naphthyl amine, p-isopropoxy-diphenyl-amine, diphenyl-p-phenylene diamine, and the like. These additives may be used in an amounts of usually 0 - 20 %, preferably 0 - 5%, based on the weight of the adhesive.

If necessary, one or more organic inert solvents, such as methyl ethyl ketone, acetone, toluene, xylene, ethyl acetate, dimethylformamide and the like, may be added to dilute and reduce viscosity of adhesives.

The amount of surgical adhesive in surgical adhesive sheet of the invention, which may vary in accordance with the part to be applied and application purpose, is usually 10 - 10,000 g/m^2, preferably 100 - 5,000 g/m^2.

Surgical adhesive sheets can be produced by various methods, for instance, by direct coating of adhesive onto sheet, by coating adhesive onto release paper followed by transferring the coating to sheet, by coating adhesive continuously or intermittently, by covering adhesive-coated surface with release paper or the like to obtain adhesive sheet having a backing of release paper or the like, or by other methods known in production of pressure-sensitive adhesives. These methods can be applied to any sheet of non-biodegradable ones and biodegradable ones. Adhesive can be applied to sheet on one side or on both sides, with any known application means, such as by using brushes, tweezers, applicators, specially-designed spatula or syringes or the like, or by spray coating using innert gases, such as nitrogen, Freons or the like.

Surgical adhesive sheets may have any shape and size, for example, large ones of such as about 30 cm by about 30 cm in size, suitable for suture of skin and the like; small ones of such as about 2 mm by about 2 mm in size; suitable for anastomosis of arterioles, nerve and the like; and tape type ones of such as 2 mm - 10 cm in width. They can be cut into a proper size for use.

Surgical adhesive sheets of the present invention can be applied in surgery, by various application methods as follows, which may be selected depending upon the part to be applied and application purpose.

(1) Transfer methods, by applying or sticking a adhesive sheet to the affected part, followed by transfering the adhesive to the part. For example, in case where a viscera is cut with a surgical knife, profuse bleeding occurs from the cutting surface. It is necessary to carry out hemostasis is needed to prevent bleeding, which can be attained with use of a surgical adhesive sheet of the invention. In this case, the adhesive sheet is sticked all over the affected part, and then the adhesive is transferred to the part along with carrying out pressure hemostasis to complete hemostasis. Sheet materials used in the adhesive sheets for this purpose are preferably films, non-adherent to surgical adhesive, for example, those made of silicone resin or fluorine-containing resin.

(2) Reinforcing methods, by applying or sticking a composite material comprising surgical adhesive combined with sheet to the part under force or the deficit part, for reinforcement and patching up. In the case used in living tissue, it is preferred to use biodegradable sheet.

(3) Wound protection methods, by applying or sticking a surgical adhesive sheet to the wounded part of such as wound of burn, for prevention of infect and acceleration of healing. For this purpose, preferred are sheet materials, permeable to water vapor or air, which include not only continuous films, but also films having a plurality of openings therein and non-woven fabrics.

As another application, surgical adhesive sheet can be applied to skin closure and so on.

Surgical adhesives coated on sheets are cured with the presence of trace water (such as water contained in sheet material and moisture in air) to cause reduction adhesive power of surgical adhesive sheets. Therefore, it is necessary to use anhydrous ones as the sheet material and the other components, not to speak of the main components; and it is preferred to cut off air containing moisture during the preparation. Surgical adhesive sheets thus obtained can be stored for a long period of time within closed vessels capable of cutting off air and moisture.

Surgical sheets of the invention can be used for application of the surgical adhesive to the affected part, as follows. In case of a sheet in the form of a film or plate, the surgical adhesive coated on the affected part is extended (or spreaded) under pressing with the sheet all over the part to be applied, whereby hemostasis of cut section of viscera can be attained effectively. A sheet in the form of balloon can be applied for pressing and extending of the surgical adhesive on uneven affected part. These sheets can attain not only application of surgical adhesive but also hemostasis under pressing at the

same time, whereby remarkably improved curative effects of surgery can be obtained. Besides the method by extending the surgical adhesive on the affected part with the sheet, there may be mentioned a method comprising spreading the surgical adhesive on a sheet beforehand and transferring the adhesive onto the affected part. Application of surgical adhesive onto the sheet can be done by known means, for instance, by using brushes, tweezers, applicators, specially-designed spatula or syringes or the like, or by spray coating using innert gases, such as nitrogen, Freons or the like.

Surgical adhesive sheets of this invention can be applied for bonding or hemostasis of tissues, such as blood vessels, heart, lung, esophagus, stomach, kidney, spleen, pancreas, duodenum, small intestine, large intestine, nerve, rectum, skin, and the like.

Treating methods using sheets of the invention are illustrated bellow in accordance with Figures.

Fig.2 shows hemostasis treatment of a viscera after cutting, with use of a surgical sheet of plate form. Fig.2 (a) shows cutting of a viscera (2) cut with a surgical knife (3). Fig.2(b) shows section (4) of the viscera (2) clamped with application of fluorine resin-coated forceps (5). As shown in Fig.2 (c), a surgical adhesive (6) is coated on a surgical sheet in the form of plate (7). As shown in Fig.2 (d), the plate (7) is pressed to the section of the viscera (2) to carry out hemostasis. Fig.2 (e) shows the stanched section (8) of the viscera (2), from which the plate (7) and the forceps (5) have being removed after curing of the surgical adhesive.

Fig.3 shows hemostasis treatment of a partly torn viscera, with use of a surgical sheet of balloon form. Fig. 3 (a) shows a partly torn viscera (9) and a sheet in the form of balloon (10). A surgical adhesive is coated on the surface of the balloon (10), and the balloon (10) is pressed to the torn part of the viscera, as shown in Fig.3 (b) to perform hemostasis. As the balloon is capable of being deformed following to the torn part of the viscera, hemostasis is easily attained.

Fig.6 shows anastomosis of blood vessels, with use of an instrument for anastomosis.

1) Into a blood vessel (14), the tip of an instrument of tapered rod (15) is inserted, as shown in Fig.6 (a). (Only a part of the rod is inserted into the vessel, and the rest of the rod remains out of the vessel.)
2) Then, surgical adhesive (16) in the form of a surgical adhesive sheet according to the invention is coated all around the vessel (14) and the rod (15) at the part where the rod is inserted into the vessel, as shown in Fig. 6 (b).
3) After the adhesive has been cured into solid, the rod (15) is taken out of the vessel to obtain a vessel, the end of which has been fixed with the cured adhesive.
4) The cured adhesive (16) is cut together with the vessel, using a surgical knife or scissors to expose the section (18) of the vessel (14) fixed within the section (17) of the cured adhesive (16), as shown in Fig.6 (c).
5) Another blood vessel is treated in the same manner.
6) The two sections of vessels thus fixed are put together, as shown in Fig.6 (d), and then joined together by applying arround them surgical adhesive and/or suture.

Having generally described the invention, a more complete understanding can be obtained by reference to certain specific examples, which are included for purposes of illustration only and are not intended to be limiting unless otherwise specified.

In the following, EO represents ethyleneoxide, PO represents propyleneoxide, and PTMG represents polytetramethyleneglycol. Urethane prepolymers were prepared by mixing under stirring polyisocyanate with polyether polyol dehydrated under reduced pressure and reacting them at a temperature of 80 degrees C for 8 hours. Parts and % in Examples and Comparative Examples represent parts by weight and % by weight, respectively. Surgical adhesives used in Examples and Comparative Examples are as follows:

1) Adhesive A1 : a surgical adhesive comprising an NCO-terminated hydrophilic urethane prepolymer having an NCO-content of 2.5%, obtained by reacting a polyether polyol [a EO/PO random copolymer having an average M.W. of 3,000 and oxyethylene content of 80%] with OCN-$CH_2(CF_2)_4CH_2$-NCO.
2) Adhesive A2: a surgical adhesive comprising an NCO-terminated hydrophilic urethane prepolymer having an NCO-content of 3.4%, obtained by reacting a polyether polyol [a EO/PO random copolymer having an average M.W.of 4,000 and oxyethylene content of 60%] with OCN-$CH_2(CF_2)_4CH_2$-NCO.
3) Adhesive A3: a surgical adhesive comprising an NCO-terminated hydrophilic urethane prepolymer having an NCO-content of 5.1%, obtained by reacting a polyether polyol [a PTMG/EO block copolymer having an average M.W. of 2,000 and oxyethylene content of 50%] with PPDI (p-phenylene diisocyanate.
4) Adhesive A4: a surgical adhesive comprising an NCO-terminated hydrophilic urethane prepolymer having an NCO-content of 3.4%, obtained by reacting a polyether polyol [a EO/PO random copolymer having an average M.W. of 4,000 and oxyethylene content of 60%] with PPDI.

Example 1

A fluorine resin sheet (1.5 mm thick) was coated with Adhesive A1 (coating amount: 400 g/m^2) to obtain a surgical adhesive sheet.

Liver of a dog was clamped with forceps in accordance with an immaginal cutting line of about 2 cm length, and cut along with the inside of the forceps. The above

surgical adhesive sheet was pressed to all over the section; and, after 5 minutes, the fluorine resin sheet was removed therefrom and the adhesive was transferred to the affected part. Whole the section was sealed completely and perfect hemostasis was attained, with very convenient handleability.

Example 2

A non-woven fabric sheet (about 5 mm thick) comprising a copolymer of lactic acid and glycolic acid was coated with Adhesive A2 (coating amount: 300 g/m^2) to obtain a surgical adhesive sheet.

Spleen of a dog was clamped with forceps in accordance with an immaginal cutting line of about 2 cm length, and cut along with the inside of the forceps. Pressure hemostasis was carried out for 5 minutes with use of the above surgical adhesive sheet to all over the section, followed by removing the forceps therefrom. The section and the surgical adhesive sheet were integrated, and perfect hemostasis was attained, with very convenient handleability.

Example 3

A polyurethane film (30 µm thick) was coated with a solution of 10 parts of Adhesive A1 diluted with 10 parts of ethyl acetate (coating amount: 400 g/m^2) to obtain a surgical adhesive sheet.

This surgical adhesive sheet was used for anastomosis for cut out parts of skin of rabbit back. The edges were placed closed to each other, and stuck together with the above adhesive sheet. After a week, the urethane film was peeled off. After 8 weeks, there was attained good cure of the affected part, without leaving substantial scar of the cut out parts. Very convenient handleability was also obtained.

Example 4

A non-woven fabric sheet (30 µm thick) composed of a polyglycolic acid was coated with Adhesive A1 in an amount of 100 g/m^2, followed by coating the surface with silver sulfadiazine as an bactericide to obtain a surgical adhesive sheet.

Mouse loss of skin (1 cm x 1 cm) was formed surgically; and, after inoculation with Pseudomonas aeruginosa, the above surgical adhesive sheet was sticked thereto. After 8 weeks, there was attained good cure of the affected part, without impediment by infection.

Example 5

Forceps and pincers made of stainless steel were surface-coated with a fluorine resin

A plate made of a fluorine resin was prepared to obtain a surgical sheet according to the invention.

Spleen of a dog was clamped with the above forceps in accordance with an immaginal cutting line of about 2 cm length, and cut along with the inside of the forceps. The above fluorine resin plate of the invention was coated with Adhesive A1, and pressed to all over the section. After 5 minutes, the plate was removed therefrom and the adhesive was transferred to the affected part. Whole the section was sealed completely and perfect hemostasis was attained. Though the adhesive had been adhered to the forceps, the pincers and the plate, they were removed with no particular resist-ance, without injuring the affected part, and no bleeding was occurred any more. By using such a sheet surgical adhesive can be dealt with very conveniently, in spite of its high viscosity.

Example 6

Forceps and pincers made of stainless steel were surface-coated with a fluorine resin.

A balloon made of a silicone resin was prepared to obtain an surgical sheet according to the invention.

Liver of a dog was clamped with the above forceps in accordance with an immaginal cutting line of about 4 cm length; and cut off, making brakes, along with the inside of the forceps. The above silicone resin balloon of the invention was coated with Adhesive A4, and pressed to all over the section of the liver. After 5 minutes, the balloon was removed therefrom and the adhesive was transferred to the affected part. The whole section was sealed completely and perfect hemostasis was attained. Though the adhesive had been adhered to the forceps, the pincers and the balloon, they were removed with no particular resistance, without injuring the affected part, and no bleeding occurred any more. By using such sheets, surgical adhesive can be dealt with very conveniently, in spite of its high viscosity.

Surgical adhesive sheets of the present invention make it possible to apply only a necessary amount to a fixed place to be bound, by cutting the sheet into a desired size; and, as compared with surgical adhesives of the prior art, a remarkable improvement in handleability can be attained by this invention. There can be exhibited, in the place of medical treatment, considerable effects in reliability and reduction of operation time, without necessity of any special instruments and techniques. In addition, surgical adhesive sheets of the invention, in which surgical adhesive is used not alone but combined with sheet into composite, make it possible applying to operations in the form not as mere bonding material but as reinforcing materials, such as patch treatment for parts broken off.

Surgical adhesives, which have high viscosity and have heretofore been of poor handleability and difficult to be applied to a fixed place to be bound in only a necessary amount, can be easily treated and applied to a fixed place to be bound in only a necessary amount, by using the sheets of this invention, particularly those in the form of films, plates and balloons.

Surgical adhesive sheets of the invention, coated or lined with material non-adherent to urethane prepoly-

mer, can be easily removed from the adhesive and the affected parts without resistance, even when the adhesive is adhered to the affected parts, so instruments can be used without fear of reblooding by force to the affected parts.

Application of adhesive sheets of the invention to surgical operation, or application of surgical adhesive with use of surgical sheets of the invention makes it possible to perform operation with adhesion, instead of suturing in conventional operation. There can be attained remarkable improvements in medical technology, such as hemostasis, prevention of leaking emzyme from viscera or the like, prevention of minute bood bessel occusion, and nerve anastomosis, as well as provisional fixing before suturing, and ensuring of bonding by combination of adhesion with suturing. Furthermore, the invention can provide high reliance and high efficiency, not only in operation, but also in medical treatment at large, for example, joining of incised wound or culting portions, adhesive treatment in dental surgery, curative means by controled release of drugs in combination with physiologically active materials, and so on.

Claims

1. A surgical adhesive sheet comprising an anhydrous sheet material coated with a surgical adhesive comprising an NCO-terminated urethane prepolymer.

2. A sheet according to claim 1 wherein the prepolymer has an isocyanate content of 1 to 10% by weight.

3. A sheet according to claim 1 or 2 wherein the prepolymer is derived from at least one organic polyisocyanate and a polyol component comprising at least one hydrophilic polyether polyol having an oxyethylene content of at least 30%.

4. A sheet according to claim 3 wherein the polyol component has an equivalent weight (average) of 100 to 5,000 and a functionality (average) of 2 to 8.

5. A sheet according to claim 3 or 4 wherein the polyisocyanate is at least one of aromatic polyisocyanates containing 6 to 20 carbon atoms, aliphatic polyisocyanates containing 2 to 18 carbon atoms, alicyclic polyisocyanates containing 4 to 15 carbon atoms, araliphatic polyisocyanates containing 8 to 15 carbon atoms, except carbon atoms in NCO groups, and modified polyisocyanates of these polyisocyanates containing one or more of urethane, carbodiimide, allophanate, urea, biuret, urethdione, urethimine, isocyanurate and oxazolidone groups.

6. A sheet according to any one of claims 3 to 5 wherein the polyisocyanate comprises a fluorine- containing polyisocyanate.

7. A sheet according to any one of claims 1 to 6 wherein the sheet material is a biodegradable sheet material.

8. A sheet according to claim 7 wherein the biodegradable sheet material comprises at least one polymer, being at least one of polyamino acids, polyamino acid copolymers, oxidized celluloses, chitin, chitin derivatives, collagen, collagen derivatives, polyacetic acids, polyglycolic acids, copolymers of lactic acid and glycolic acid and polymers of hydroxylbutyric acid.

9. A sheet according to any one of claims 1 to 6 wherein the sheet material is a non-absorbing sheet material comprising at least one polymer, being at least one of olefinic polymers, acrylic and methacrylic resins, hydroxyl-containing polymers, halogen-containing resins, diene polymers, polyesters, polycarbonates, polyamides, polyimides, polyurethane resins and silicone resins.

10. A sheet according to claim 10 wherein the non-absorbing sheet material comprises a film of silicone resin or fluorine-containing resins.

11. A sheet according to claim 10 wherein the non-absorbing sheet material comprises a film of silicone resin or fluorine-containing resin which is non-adherent to the surgical adhesive.

12. A sheet according to claim 9, 10 or 11 in the form of a film, plate or balloon comprising a non-absorbent material non-adherent to an NCO- terminated urethane prepolymer coated with a surgical adhesive comprising an NCO- terminated urethane prepolymer.

Patentansprüche

1. Chirurgische Haftfolie, umfassend ein wasserfreies Folienmaterial, welches mit einem chirurgischen Klebstoff beschichtet ist, der ein NCO-terminiertes Urethan-Vorpolymer umfaßt.

2. Folie gemäß Anspruch 1, wobei das Vorpolymer einen Isocyanatgehalt von 1 bis 10 Gew.-% aufweist.

3. Folie gemäß Anspruch 1 oder 2, wobei das Vorpolymer von mindestens einem organischen Polyisocyanat und einer Polyolkomponente, welche mindestens ein hydrophiles Polyetherpolyol mit einem Oxyethylengehalt von mindestens 30% umfaßt, abgeleitet ist.

4. Folie gemäß Anspruch 3, wobei die Polyolkomponente ein Äquivalentgewicht (Mittel) von 100 bis 5.000 und eine Funktionalität (Mittel) von 2 bis 8 besitzt.

5. Folie gemäß Anspruch 3 oder 4, wobei das Polyisocyanat mindestens eines ist aus: aromatischen Polyisocyanaten, welche 6 bis 20 Kohlenstoffatome enthalten, aliphatischen Polyisocyanaten, welche 2 bis 18 Kohlenstoffatome enthalten, alicyclischen Polyisocyanaten, welche 4 bis 15 Kohlenstoffatome enthalten, araliphatischen Polyisocyanaten, welche 8 bis 15 Kohlenstoffatome enthalten, außer den Kohlenstoffatomen in NCO-Gruppen, und modifizierten Polyisocyanaten dieser Polyisocyanate, welche eine oder mehrere von Urethan-, Carbodiimid-, Allophanat-, Harnstoff-, Biuret-, Urethdion-, Urethimin-, Isocyanurat- und Oxazolidongruppen enthalten.

6. Folie gemäß einem der Ansprüche 3 bis 5, wobei das Polyisocyanat ein Fluorenthaltendes Polyisocyanat umfaßt.

7. Folie gemäß einem der Ansprüche 1 bis 6, wobei das Folienmaterial ein bioabbaubares Folienmaterial ist.

8. Folie gemäß Anspruch 7, wobei das bioabbaubare Folienmaterial mindestens ein Polymer umfaßt, welches mindestens eines ist von: Polyaminosäuren, Polyaminosäurecopolymeren, oxydierten Cellulosen, Chitin, Chitinderivaten, Kollagen, Kollagenderivaten, Polyessigsäuren, Polyglcolsäuren, Copolymeren von Milchsäure und Glycolsäure und Polymeren von Hydroxybuttersäure.

9. Folie gemäß einem der Ansprüche 1 bis 6, wobei das Folienmaterial ein nicht-absorbierendes Folienmaterial welches mindestens ein Polymer umfaßt, das mindestens eines ist von: olefinischen Polymeren, Acryl- und Methacrylharzen, Hydroxyl-enthaltenden Polymeren, Halogen-enthaltenden Harzen, Dienpolymeren, Polyestern, Polycarbonaten, Polyamiden, Polyimiden, Polyurethanharzen und Silikonharzen.

10. Folie gemäß Anspruch 10, wobei das nicht-absorbierende Folienmaterial einen Film aus Silikonharz oder Fluor-enthaltenden Harzen umfaßt.

11. Folie gemäß Anspruch 10, wobei das nicht-absorbierende Folienmaterial einen Film aus Silikonharz oder Fluor-enthaltendem Harz umfaßt, welches auf dem chirurgischen Klebstoff nicht haftet.

12. Folie gemäß Anspruch 9, 10 oder 11 in der Form eines einer Platte oder eines Ballons, umfassend ein nicht-absorbierendes Material, welches aufeinem NCO-terminierten Urethan-Vorpolymer, beschichtet mit einem chirurgischen Klebstoff, der ein NCO-terminiertes Urethan-Vorpolymer umfaßt, nicht haftet.

Revendications

1. Feuille adhésive chirurgicale comprenant un matériau anhydre en forme de feuille enduit d'une colle chirurgicale comprenant un prépolymère à base d'uréthanne se terminant par NCO.

2. Feuille selon la revendication 1, dans laquelle la teneur du prépolymère en isocyanate est de 1 à 10 % en poids.

3. Feuille selon la revendication 1 ou 2, dans laquelle le prépolymère est dérivé d'au moins un polyisocyanate organique et d'un composant de type polyol comprenant au moins un polyéther polyol hydrophile dont la teneur en oxyéthylène est au moins égale à 30 %.

4. Feuille selon la revendication 3 dans laquelle le poids de combinaison (en moyenne) du composant de type polyol est de 100 à 5 000 et le nombre de groupes fonctionnels (en moyenne) est de 2 à 8.

5. Feuille selon la revendication 3 ou 4, dans laquelle le polyisocyanate est choisi parmi au moins les polyisocyanates aromatiques contenant de 6 à 20 atomes de carbone, les polyisocyanates aliphatiques contenant de 2 à 18 atomes de carbone, les polyisocyanates alicycliques contenant de 4 à 15 atomes de carbone, les polyisocyanates araliphatiques contenant de 8 à 15 atomes de carbone, sans tenir compte des atomes de carbone des groupes NCO, et les polyisocyanates modifiés dérivés de ces polyisocyanates contenant un ou plusieurs groupes de type uréthanne, carbodiimide, allophanate, urée, biuret, uréthdione, uréthimine, isocyanurate et oxazolidone.

6. Feuille selon l'une quelconque des revendications 3 à 5, dans laquelle le polyisocyanate comprend un polyisocyanate fluoré.

7. Feuille selon l'une quelconque des revendications précédentes, dans laquelle le matériau en forme de feuille est un matériau biodégradable en forme de feuille.

8. Feuille selon la revendication 7, dans laquelle le matériau biodégradable en forme de feuille comprend au moins un polymère choisi parmi au moins les acides polyamino, les copolymères d'acides polyamino, les celluloses oxydées, la chitine, les dérivés de la chitine, le collagène, les dérivés du collagène, les acides polyacétiques, les acides polyglycoliques, les copolymères de l'acide lactique et de l'acide glycolique et les polymères de l'acide hydroxybutyrique.

9. Feuille selon l'une quelconque des revendications 1 à 6, dans laquelle le matériau en forme de feuille est un matériau en forme de feuille non adsorbant comprenant au moins un polymère choisi parmi au moins les polymères oléfiniques, les résines acryliques et méthacryliques, les polymères hydroxylés, les résines halogénées, les polymères diéniques, les polyesters, les polycarbonates, les polyamides, les polyimides, les résines polyuréthaniques et les résines silicones.

10. Feuille selon la revendication 10, dans laquelle le matériau en forme de feuille non adsorbant comprend une pellicule de résine silicone ou de résines fluorées.

11. Feuille selon la revendication 10, dans laquelle le matériau en forme de feuille non adsorbant comprend une pellicule à base de résine silicone ou une résine fluorée qui n'adhère pas à la colle chirurgicale.

12. Feuille selon la revendication 9, 10 ou 11 en forme d'une pellicule, d'une lame ou d'un ballonnet comprenant un matériau non adsorbant qui n'adhère pas au prépolymère à base d'uréthanne se terminant par NCO et enduit d'une colle chirurgicale comprenant un prépolymère à base d'uréthanne se terminant par NCO.

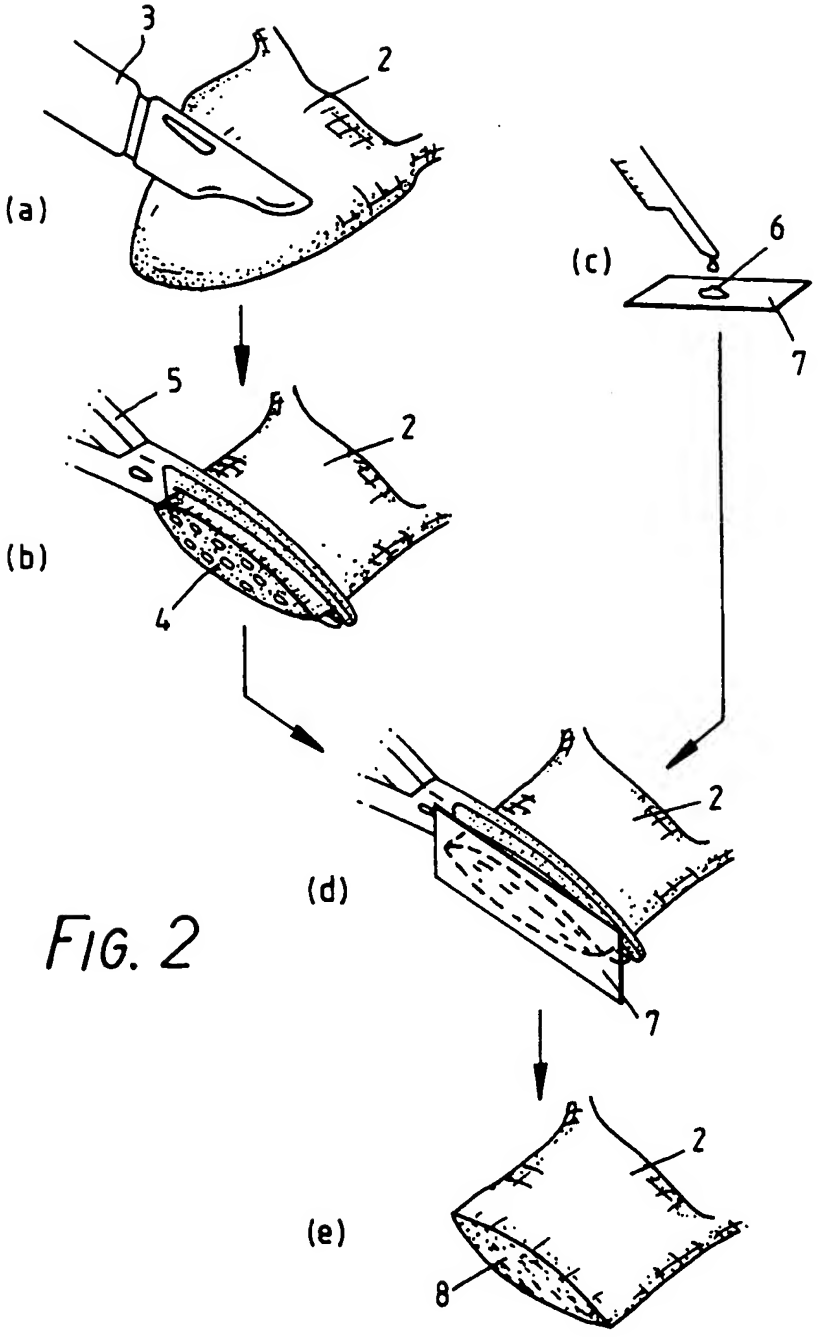

FIG. 2

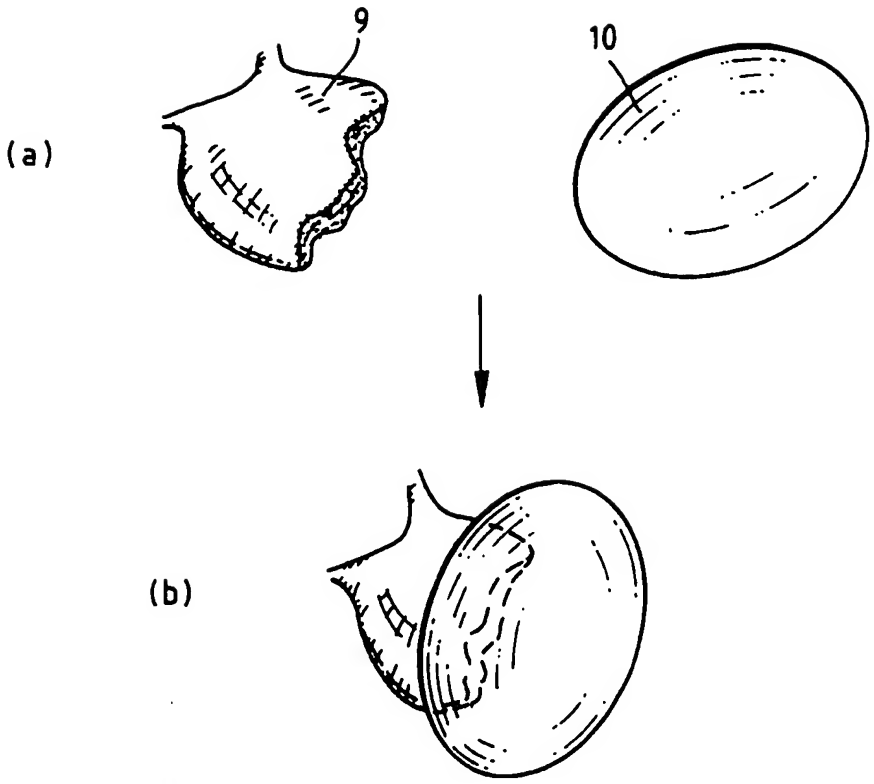

FIG. 3

FIG. 6